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A. KABATA-PENDIAS *

LEACHING OF CERTAIN TRACE ELEMENTS FROM COLUMNS WITH RENDZINA SOIL

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Soil columns were used to study the movement of certain micronutrients through calcareous soil material as influenced by the leaching with different extractants. The most appreciable amounts af all trace elements were mobilized by acetic acid and ammonium oxalate solutions. In the dissolution of micronutrients by plant extracts polyphenols play an important role. The leaching of these elements with chemical solvents is related mostly to cation exchange reactions and chemical dissolution.

Laboratory simulation of the mobilization of trace element in soils is not an easy task, because the natural processes which are occuring in the field are complex and difficult to duplicate in the laboratory. The main solvents present in soils are aqueous extracts of plant material and water with carbonic acid and some ions dissolved. Both kinds of the solvents are capable of causing the non-biological dissolution of the cations. The mobilization of the cations, involving the transportation and redeposition of chemical constituents play an important role in the distribution of micronutrients within soil profiles and in their availability to plants. According to the investigations of Kee and Bloomfield [7, 8], as well as to the results obtained by Hodgson *et al.* [3, 4], reactions of cation complexing are the most important in these phenomena.

The laboratory experiment of leaching of trace elements, using different solvents, was conducted in order to investigate the behavior of several micronutrients in the soil columns. Used solvents similar to those occuring in natural soils should under suitable conditions bring about changes analogous to these obtained in the field.

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* Doc. dr Alina Kabata-Pendias — Institute of Soil Science and Plant Cultivation, Osada Pałacowa, Puławy, Poland.

EXPERIMENTAL PROCEDURE

Calcareous soil material (800 g) was introduced with the help of water, into glass cylinders of about 6 × 35 cm inside dimension. The samples were taken from the distinquished horizons of brown rendzina derived from Cretaceous limestone (located near Łysaków voivodship Kielce). Detailed description of this soil is given elsewhere [6]. The soil columns were exposed to a slow flow of the leaching liquids, at a rate ranging from 1 to 20 ml per hour. However, it was impossible to regulate the rate of flow and percolation for each soil column because of the different drainage condition of the soil cores.

The following extractants were used:

I. Aqueous extract of oak leaves, pH 4.8
II. Aqueous extract of pine needles, pH 4.4
III. Aqueous extract of lupine, pH 5.1
IV. Tamm's solution, pH 3.2, 0.2 M ammonium oxalate
V. Water saturated with CO_2, pH 4.0
VI. Acetic acid, 2.5%, pH 2.5

The experiment was conducted for three months. The percolating liquids were collected every 2 days for the first 10 days, and every 10 days for the next period of the experiment. Content of certain elements in the obtained solutions was determined by the spectrophotometric methods [5].

When the experiment was terminated, the columns were allowed to drain and were frozen. After the removal of glass tubes the soil cores were bisected horizontally and samples representing the distinquished horizon from the same depths of each soil column were taken for laboratory examination.

RESULTS AND DISCUSSION

One has to recognize that it is impossible to reproduce all natural soil conditions with a leaching experiment conducted in laboratory. Nevertheless, the open system of this experiment most closely resemble the condition in soils. The behavior of some trace elements under these conditions was investigated.

During the relatively short time of the experiment (3 months) it has been shown that the leaching of a calcareous soil material, with different extractants, can result in the dissolution and redeposition of several chemical elements and in the development of profiles with defined zones. The differences within the soil columns corresponded to the types of percolating liquids used and are described in other publication [6].

The influence of the used liquids on micro-organisms in soil material was also examined. The most active growth of bacteria and actinomycetes was found in the medium with lupine extract. The amounts of micro-organisms in the oak leaf and pine needle extracts were moderate, however an increase of fungi was observed. All other liquids were harmful to micro-organisms. The micro-biological activity in the soil and rock samples was determined during the final stages of the experiment (Tab. 1). To check a very intense growth of fungi in the cylinders containing A_1 horizon an aseptic solution was added, at the beginning of the experiment. For this reason the figures obtained for this part of the experiment were lowered, especially in respect to fungi. Nevertheless, there is observed a very intense growth of all micro-organisms in the soil columns including these with limestone, leached with plant extracts.

TABLE 1. MICRO-ORGANISMS IN SOIL MATERIAL AT THE TERMINATION OF EXPERIMENT (IN THOUSAND PER 1 G)

Horizon	Extractant	Bacteria	Actinomycetes	Fungi
A_1	I	7 000	158	518.00
	II	16 600	7 400	2.13
	III	58 200	11 400	0.36
	IV	28	27	0.02
	V	4 820	1 740	0.12
	VI	1 828	0	0
(B)	I	618 600	0	22.70
	II	84 280	0	13.00
	III	3 930 000	0	4.50
	IV	830	0	5.00
	V	17 100	1 200	0.90
	VI	4 880	0	0
C	I	27 000	600	2.85
	II	4 900	0	960.00
	III	722 700	0	3.70
	IV	75	0	0
	V	576	0	0
	VI	274	0	43.60

In all soil columns treated by different extractants the rate of dissolution of micronutrients from the A_1 horizon was more slowly than from the (B) and C one. Nevertheless the total amounts of the extracted elements were a few times higher for the A_1 horizon (Tab. 2). In the columns with the (B) and C horizons almost all elements were mobilized in appreciable amounts during the first 10 days of experiment what corresponds to the first liter of the percolating liquids. Later extraction of these elements was rather negligible. On the other hand, there was observed continuous increase of extracted amounts of all trace elements from A_1 horizon with the flow of liquids up to about 3.5 liters or more, depending on the type of solution.

TABLE 2. THE LEACHING OF TRACE ELEMENTS FROM SOIL MATERIAL (IN PPM)

	Soil horizon	Mn	Zn	Cu	Ni	Co	Mo	B
Total content of soil material	A_1	380.00	290.10	25.50	25.00	6.35	2.80	12.50
	(B)	225.00	140.12	30.00	20.50	8.52	1.82	8.50
	C	110.00	72.00	21.20	43.50	4.20	1.30	7.00
Extractant used:								
I	A_1	19.16	3.05	0.73	0.26	0.98	0.07	0.37
	(B)	3.57	2.77	5.48	0.14	0.07	0.04	0.23
	C	2.16	3.73	0.64	0.12	0.09	0.03	0.51
II	A_1	47.01	8.94	1.14	0.37	0.23	0.06	0.44
	(B)	7.93	2.40	0.67	0.10	0.06	0.04	0.26
	C	11.39	3.44	0.68	0.09	0.06	0.03	0.35
III	A_1	37.68	12.98	1.46	0.84	0.18	0.05	0.38
	(B)	6.07	2.91	0.79	0.24	0.07	0.07	0.34
	C	1.94	3.33	0.75	0.21	0.17	0.03	0.31
IV	A_1	51.38	14.78	3.79	3.00	0.74	0.32	0.38
	(B)	14.50	4.14	1.12	1.60	0.27	0.16	0.37
	C	2.25	4.59	0.85	0.24	0.15	0.04	0.16
V	A_1	36.03	16.65	1.78	0.45	0.18	0.09	0.78
	(B)	13.96	5.59	1.17	0.34	0.17	0.14	0.46
	C	1.25	4.45	0.46	0.08	0.04	0.03	0.25
VI	A_1	167.03	19.91	3.75	1.76	1.05	0.03	0.72
	(B)	79.30	7.36	2.86	1.53	1.00	0.04	0.91
	C	14.60	6.80	1.63	0.04	0.25	0.03	0.78

Although the initial pH of extractants was different there was observed in almost all cases a rapid decrease of its value during the first days of the experiment and later slowly increase. Only in the soil columns treated with acetic acid, pH of the percolating solution was kept constant at about 2.5 after a small growth at the beginning.

According to Gad and Le Rich [2] ammonium oxalate dissolves high quantities of trace elements, especially when the soil samples are without organic matter. In this experiment the total amounts of the extracted micronutrients by ammonium oxalate solution were often higher than those leached out by other investigated liquids, with the exception of ~~an~~ acetic acid solutions. Zinc only was mobilized to a visible degree in all the soil horizon at a further stage of leaching and seems to be connected with the decomposition of some resistant zinc compounds.

Acetic acid is a commonly used solution to determine the availability of several micronutrients, especially cobalt, copper and zinc. The dissolution of almost all trace elements exposed to the leaching with acetic acid, was relatively speaking the greatest when compared with all other examined liquids. These phenomena are certainly related to the high volume of the extractant passed through the cylinders with soil. The concentration of trace elements extracted from leached soil columns per 1 liter of solution is not higher for acetic acid than for all other liquids (Tab. 3).

TABLE 3. TRACE ELEMENTS EXTRACTED FROM SOIL COLUMNS IN γ PER 1 LITER OF SOLUTIONS

Extractant	Soil horizon	Mn	Zn	Cu	Ni	Co	Mo	B
I	A_1	3830	610	150	50	200	10	80
	(B)	926	680	140	40	20	11	60
	C	360	620	105	15	15	3	84
II	A_1	8000	1520	200	60	40	10	70
	(B)	2413	710	150	30	20	13	70
	C	1340	404	79	10	10	3	41
III	A_1	15070	5160	580	340	70	20	150
	(B)	1517	710	190	60	17	7	90
	C	330	566	117	37	31	5	54
IV	A_1	6850	1979	510	400	100	430	50
	(B)	2985	820	220	320	55	33	70
	C	194	395	73	21	13	3	14
V	A_1	1100	510	60	14	6	3	2
	(B)	425	170	35	10	5	4	14
	C	116	425	44	7	3	2	23
VI	A_1	4310	510	100	45	30	0.7	20
	(B)	2135	200	78	41	27	1	25
	C	1407	656	156	36	23	2	84

Although amounts of the extracted microelements have differed for each horizon leached with the different extractants, general orders of dissolution based on their percentage solubility could be presented:

A_1 horizon: $Mn > Zn > Cu > Mo > Co > B > Ni$
(B) horizon: $Mn > Mo > B > Cu > Zn > Co > Ni$
C horizon: $Zn > Mn > Cu > Mo > B > Co > Ni$

In general, the solubility of all trace elements was rather low and did not exceed 10 per cent of their total content in soil material. The only exception was acetic acid solution which has extracted a higher proportion of manganess.

Distribution of micronutrients within the soil columns after the termination of the experiment was calculated as values of index of distribution. Micronutrients are know to form soluble complexes with different agents, especially with polyphenols [1, 9] and they can be expected to be translocated during the experiment described. Nevertheless, manganesse and partly zinc appear to be accumulated in the upper zones of soil columns treated by plant extracts. Copper, cobalt and nickel were leached down with almost all liquids and were concentrated rather in lower zones of soil cores. Molybdenum behaved in a more complicated fashion and was strongly leached out, but was also accumulated in some zones of soil cores. In general, manganese, zinc and molybdenum were removed in a higher degree from A_1 horizon than from the (B) one. It is related to the soluble organic complexes which occurred mainly in the A horizon. In many cases, nickel was the least and manganese was the most mobile of the elements. With few exceptions more appreciable amounts of micronutrients were dissolved by pine needle and lupine than by oak leaf exctract, and by acetic than by other chemical solvents. However, in respect to trace element concentration per 1 liter of extractants, Tamm's solution appears to be the most active one and CO_2-water the least active solvent.

In the dissolution of micronutrients by plant extracts polyphenols from plant material and those biosynthesized by micro-organisms play an important role. On the other hand, the leaching of these elements with chemical solvents is related mostly to cation exchange reactions and chemical dissolution processes.

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ROZPUSZCZALNOŚĆ NIEKTÓRYCH PIERWIASTKÓW ŚLADOWYCH POD WPŁYWEM ŁUGOWANIA RĘDZINY UMIESZCZONEJ W CYLINDRACH

Przeprowadzono doświadczenie na kolumnach glebowych celem badania rozpuszczalności mikroelementów pod wpływem różnych roztworów ługujących. Roztwory kwasu octowego i Tamma powodowały największe uruchomienie badanych składników. Polifenole występujące w wyciągach z materiału roślinnego odgrywały bardzo istotną rolę w procesach ługowania mikroelementów. Przy traktowaniu gleby wodnymi roztworami związków chemicznych zachodziły nie tylko reakcje wymiany kationów, ale także procesy związane z przeobrażeniami glinokrzemianów.

Translator: The Author